RI 9406

REPORT OF INVESTIGATIONS/1992

Vapor-Phase Reactions To Prepare Titanium Nitride Powder

By G. J. Slavens

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
cm	centimeter	mL/min	milliliter per minute
ft	foot	μm	micrometer
g/cm³	gram per cubic centimeter	μm Hg	micrometer of mercury
h	hour	μm Hg/min	micrometer of mercury per minute
in	inch	mol	mole
K	kelvin	MPa	megapascal
kcal/mol	kilocalorie per mole	pct	percent
kV	kilovolt	ppm	part per million
L	liter	psig	pound per square inch, gauge
L/min	liter per minute	psig/min	pound per square inch, gauge, per minute
mA	milliampere	s	second
min	minute	wt pct	weight percent

VAPOR-PHASE REACTIONS TO PREPARE TITANIUM NITRIDE POWDER

By G. J. Slavens[1]

ABSTRACT

The U.S. Bureau of Mines conducted research on preparing submicrometer titanium nitride (TiN) powder as a substitute for tungsten carbide (WC) in cutting tools and wear-resistant parts. Earlier research on a small scale was expanded to include a larger reactor. The TiN powder was produced by contacting titanium tetrachloride ($TiCl_4$) with anhydrous ammonia (NH_3) in the presence of Mg at 1,100° C. The powder was collected in an electrostatic precipitator (ESP) filled with ultra-high-purity (UHP) Ar. All collected powder was thermal vacuum distilled to remove Mg and magnesium chloride ($MgCl_2$), leaving the purified TiN. Powder handling and purification procedures were conducted to assure low oxygen content in the powder product. Oxygen content in the distilled TiN powder product was as low as 0.40 wt pct. Nitrogen averaged near 22.0 wt pct with a high of 22.4 wt pct. The purified powder product had an average median particle diameter of 0.14 μm with a standard deviation of 0.09 μm.

[1]Chemical engineer, Albany Research Center, U.S. Bureau of Mines, Albany, OR.

INTRODUCTION

Nearly half of the cutting tool industry in the United States is based on cemented WC. It is used extensively for C-5-grade cutting tools and wear-resistant parts because it possesses high hardness and abrasion resistance. Cobalt binder with titanium carbide (TiC) and tantalum carbide (TaC) additives are usually mixed with the WC, compacted, and sintered to form the desired cemented shapes (*1*).[2]

However, the United States is almost totally dependent upon critical imported materials to produce the cemented WC parts. Cobalt is considered a strategic and critical metal at high risk and W and Ta are critical materials. No adequate domestic deposits exist for these materials. To decrease the dependency on foreign sources, the U.S. Bureau of Mines has undertaken research to find substitutes for WC tools bits and wear-resistant parts. This research program has developed several different Ni-bonded TiC cermet compositions that show promise for tool bits (*2*).

TiN has also shown real promise as a WC extender and substitute. An increasing number of tool bits and inserts have had TiN coatings physically and chemically vapor deposited on the surface. This coating is very hard, which increases the wear resistance of the coated part. TiN coatings also have increased lubricity, which reduces friction, and chemical inertness, which reduces reactions with the Co binder. The result of using TiN-coated tools is improved parts finish, using lower power levels with increased cutting speeds and feed rates. The life of wear-resistant parts and cutting tools can also be extended by 3 to 10 times by using TiN coatings (*3-7*).

A U.S. patent by a Japanese company reported a method that takes TiN coatings on a WC base one step further (*8*). TiN was substituted for WC as the base material in the cutting tool cermet. Properties similar to those for cemented carbides are reported.

The wear-resistant parts and cutting tool markets are currently demanding sintered products with greater hardness, higher strength, higher strength-density ratios, and other improved properties when compared to traditional materials. However, products made from nonoxide materials, such as titanium diboride (TiB_2), TiN, and silicon nitride (Si_3N_4), have not been fully successful. Submicrometer powders are desired to produce the nonoxide parts at a lower sintering temperature while yielding a finer microstructure (*9-13*). The smaller particles have a much more uniform chemical composition, which produces a superior product. In addition, the smaller particles can be used to form near-net-shape parts, which require less machining than parts made from larger powder, resulting in twice the number of acceptable parts. However, powders of uniform size or of several specific sizes, allowing size blending, are necessary to produce high-density powder compacts without the heterogeneities that cause parts failures (*13*). The different particle sizes fill between-particle voids, giving higher packing density and improved mechanical properties. Therefore, particle size and distribution data are needed to prepare quality cermets. Parts with these improved chemical and physical properties are expensive because the submicrometer particles are expensive to produce (*13*).

Difficulties also arise with the use of submicrometer powders. The primary concern is the increased reactivity of a particle with a large surface area, which increases air contamination possibilities during handling and processing. Inhomogeneous mixing and shrinkage upon sintering are problems that also must be overcome to adequately utilize submicrometer powders.

Several techniques are used to produce nonoxide powders. These include carbothermal reduction, laser synthesis, plasma synthesis, solid-solid and solid-gas combustion syntheses, and vapor-phase synthesis (*10-11*). The Bureau initiated research to produce nonoxide powders by vapor-phase reactions. Powders produced included TiN, TiC, and titanium carbonitride [Ti(C,N)] (*14-15*). To prepare TiN, $TiCl_4$ was reduced by Mg in the presence of N_2 or NH_3 at 1,000° C. The powder products were then leached with dilute hydrochloric acid (HCl) to separate Mg and $MgCl_2$ from the TiN powder. However, the resultant powder contained 5 wt pct oxygen,[3] which are unsuitable for further processing.

The previously mentioned U.S. patent states that <1 wt pct oxygen is essential to produce TiN cermets (*8*). Impurities such as oxygen tend to segregate at the grain boundaries and form very small heterogeneities. These heterogeneities in turn can cause sudden parts failure (*13*). Oxygen found in TiN powder causes microporosity, embrittlement, and cracking and often results in poor sintering. Consequently, TiN-based sintered parts often have poor mechanical properties. The patent also states that other impurities are inevitable and should be maintained at trace levels to produce tough cermets. The exceptions to this are Fe and Cr, which must be kept at the lowest possible concentration but never above 1.5 or 0.5 wt pct, respectively (*8*).

[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

[3]Since nitrogen and oxygen atoms are found in compounds or as diatomic gases but not individually, the use of the symbols N and O can be confusing. Therefore, N_2 or O_2 will refer to the gases only and N and O will be used in compounds only. Nitrogen and oxygen will be written out in the text when referring to the elements other than as diatomic gases or when referring to all sources of the elements.

As in all cermets, TiN powder must be properly wetted by the Co and/or Ni binders to form a tough product. Various additives aid in the wetting of the powder, which improves the strength of the cermets (*8*).[4] However, preliminary studies also indicate that a 1:1 ratio of Ti to nitrogen in TiN powder is critical to maximum wetting of the TiN powder by the Ni binder.[5] Therefore, stoichiometric TiN (22.6 wt pct nitrogen) is needed to produce the highest strength sintered cermet.

This report discusses the large-scale experiments conducted by the Bureau to produce TiN powder by vapor-phase reactions. The effect of various parameters on the resultant powder, and oxygen, nitrogen, and metal impurity contents are reported. Particle size analyses and the effects of parameters on the particle size are also discussed. A study of TiN cermets was beyond the scope of this research. However, the Bureau had ongoing research to study titanium aluminum oxynitride (TiAlON) composites produced from TiN, alumina (Al_2O_3), and aluminum nitride (AlN). The TiN produced by the vapor-phase reaction was substituted into TiAlON and evaluated. The results of using TiN synthesized in the vapor phase as a component of TiAlON are included.

ACKNOWLEDGMENTS

The author is indebted to G. W. Elger, research chemist, Albany Research Center (retired), for his initial direction and insights on the equipment and progress of the research. J. L. Hoyer, ceramic engineer, and J. P. Bennett, supervisory ceramic engineer, at the Tuscaloosa Research Center were instrumental in providing data on TiAlON composites. Their contributions are also greatly appreciated.

EXPERIMENTAL EQUIPMENT AND CHEMICALS

As much as possible, the formation, collection, and handling of TiN and associated powders were done in a low-oxygen environment. Long evacuation times, UHP Ar, and high-purity reactants aided in reducing impurities, especially oxygen, in the final TiN powder product. A meter capable of measuring down to 0.1 ppm O_2 monitored all gases before exposing reactants or powders to the gaseous atmosphere. Materials of construction that were inert to the particular environment were used as much as possible. High-purity chemicals were used as feed products to ensure low impurities in the final TiN powder product.

The flowchart in figure 1 illustrates the steps in the TiN powder production process. Figure 2 shows the experimental apparatus employed in synthesizing and collecting the TiN powder, while figure 3 is a schematic of this same equipment. Figure 4 shows the distillation equipment used to purify the TiN powder. Figure 5 is a schematic of the distillation equipment. All equipment and procedures will be discussed individually.

REACTOR AND COLLECTION TRAIN

Cylinder gas was used to supply all gases to the system. Flowmeters controlled the flow rate of all these gases. UHP N_2 or anhydrous NH_3 supplied the nitrogen needed

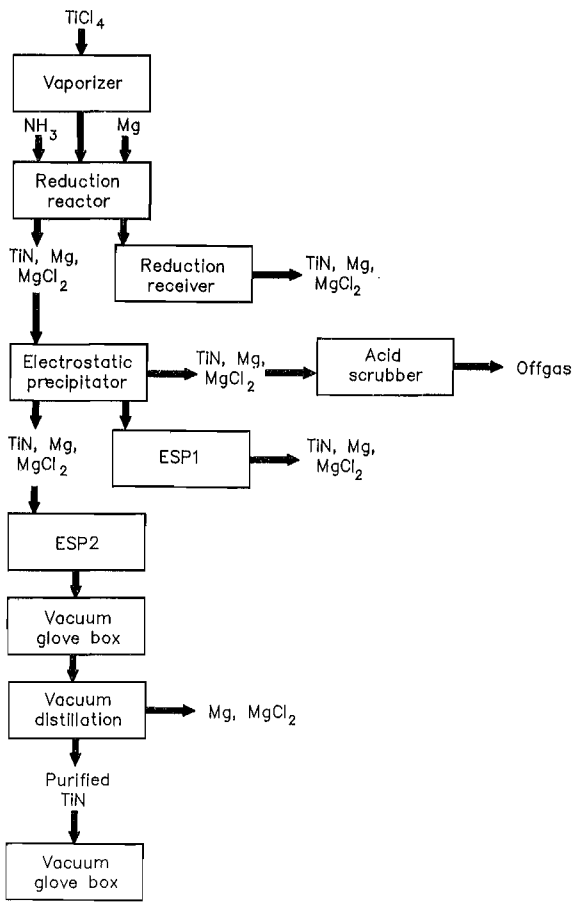

Figure 1.—Flowchart of TiN powder production process.

[4]Work done by Technical Research Associates, Inc., under Bureau of Mines contract J0145045.

[5]Work cited in footnote 4.

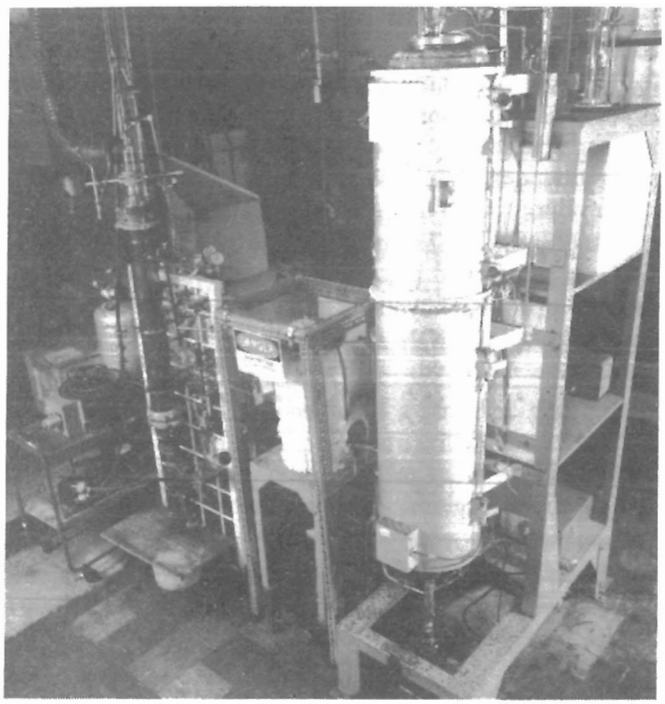

Figure 2.—Overall view of reaction and TiN powder collection systems.

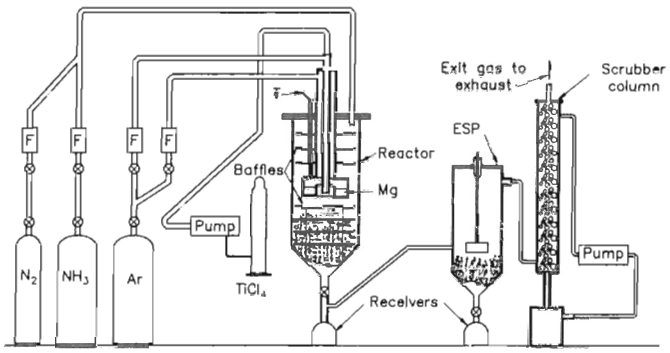

Figure 3.—Schematic diagram of experimental apparatus for synthesizing TiN powder.

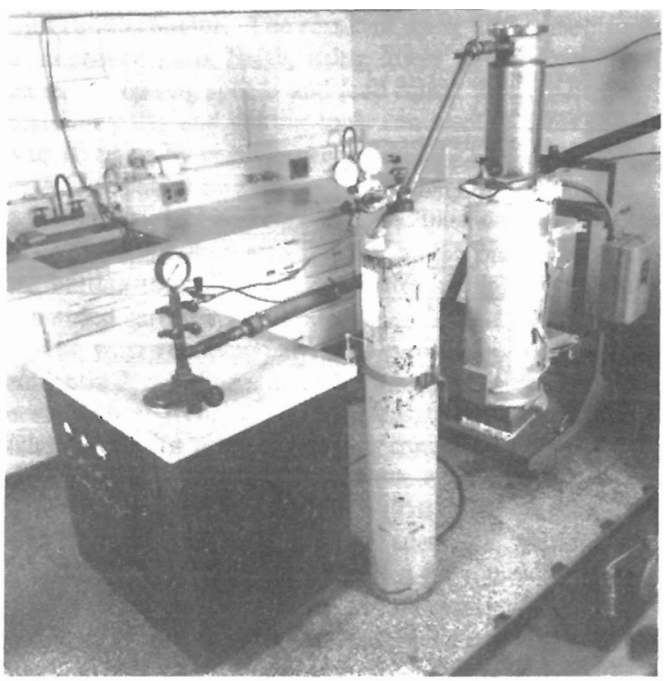

Figure 4.—Thermal vacuum distillation apparatus used to distill TiN powder.

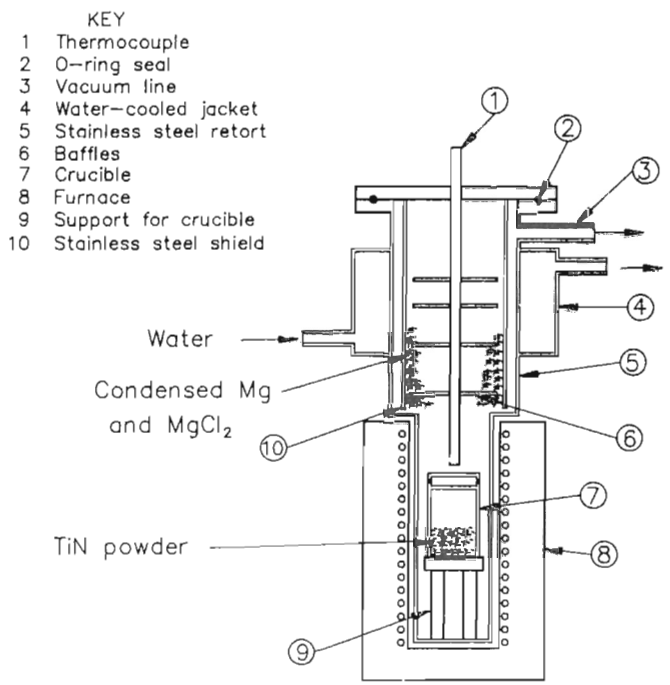

Figure 5.—Schematic diagram of experimental apparatus for distilling TiN powder.

for reaction. The UHP N_2 was 99.999 wt pct pure with specifications of <1 ppm O_2, 3 ppm H_2O, and 1 ppm total hydrocarbons (THC). Anhydrous NH_3 was 99.99 wt pct pure and contained maximum typical analyses of 10 ppm CO, 30 ppm N_2, 50 ppm O_2 and H_2O, and 10 ppm CH_4. Two different grades of Ar served to purge and protect the system during and after reaction—prepurified and UHP. Prepurified Ar had a minimum purity of 99.998 wt pct and contained <3 ppm O_2 and 3 ppm H_2O. The UHP Ar was 99.999 wt pct and had specifications of <1 ppm THC 2 ppm O_2, 6 ppm N_2, and 3 ppm H_2O. One-quarter-inch-diameter Mg rods were cut to fit into the Mg holding vessel located inside the reactor. The Mg analysis is shown in table 1. $TiCl_4$ was acquired from a major Ti sponge manufacturer. A typical chemical analysis resulted in 10 to 20 ppm Al, 10 to 100 ppm Fe, and <10 ppm B, Ca, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Si, Sn, and V. To assure its purity after months or years of storage, the $TiCl_4$ was distilled in borosilicate, heat-resistant glass before reacting. The distillation, collection, and storage of the $TiCl_4$ was done with prepurified Ar cover to assure quality.

Table 1.—Chemical analysis of Mg used for reductant, weight percent

Element	*Analysis*	*Element*	*Analysis*
Al	0.02	Ni	0.002
B	.0002	Pb	.009
Cu	.002	Si	.009
Fe	.037	Sn	.03
Mn	.016	Ti	.008
Mo	<.01		

The reactor and powder collection train were used to synthesize and collect, respectively, the powder. Figure 6 is a schematic of the reactor, which consisted of AISI Type 310 stainless steel (SS), schedule 40 pipe, 68 in long, with a 4-in diameter. The bottom was funnel shaped to direct the powder out of the reactor and into the collection train. Water cooling reduced the temperature of the exiting stream to prevent melting the plastic lines. The reactor was suspended by a flange near its top, inside two stacked, 5-in-diameter, high-temperature furnaces. The top and bottom furnaces were 2 and 3 ft high, respectively. These furnaces were resistance heated and could be independently controlled to give some temperature variation in the two heating zones of the reactor. Titanium baffles were installed inside the reactor to increase mixing of the reactants and angled to reduce powder retention (fig. 7).

The reactor top (fig. 8) was O-ring sealed and water cooled to protect the O-ring at elevated temperatures. Anhydrous NH_3 was metered into the reactor through an opening in the top—the same opening used to introduce

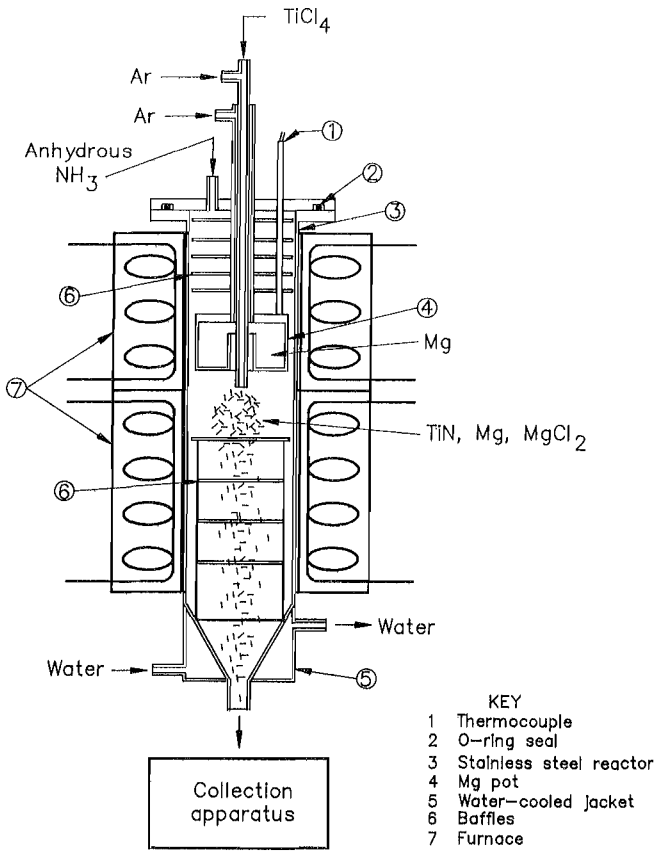

Figure 6.—Schematic diagram of experimental reduction reactor.

prepurified Ar to purge the system before and after reduction. Two concentric tubes passed through the center of the top. The inside tube was made of Al_2O_3 and carried $TiCl_4$ and UHP Ar to the reaction zone. The Ar was used to keep the discharge end of the tube free from reaction deposits. The outside tube was made of AISI Type 316 SS, with several stainless steel baffles attached to reduce the heating of the reactor top. An unalloyed Ti container was attached to the bottom of the tube to hold the Mg reductant. This container was called the Mg pot. The outside tube also delivered UHP Ar to the Mg pot and swept the Mg vapor out of the pot into the reaction zone, where it reacted with $TiCl_4$ and NH_3.

The reactor top also contained an AISI Type 316 SS thermocouple well with the lower end welded closed. The well rested in a hole drilled into, but not through, the Mg pot top. This thermocouple was used to monitor the temperature of the Mg pot during a run.

Additional thermocouples were located against the outside wall of each furnace element for temperature control. Two other thermocouples were located inside the furnace elements but outside the reactor to monitor reaction zone

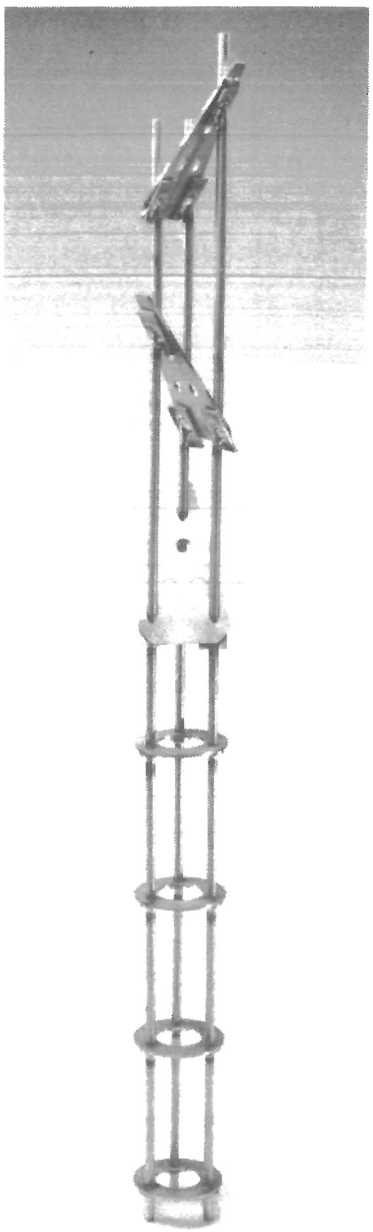

Figure 7.—Reactor baffles.

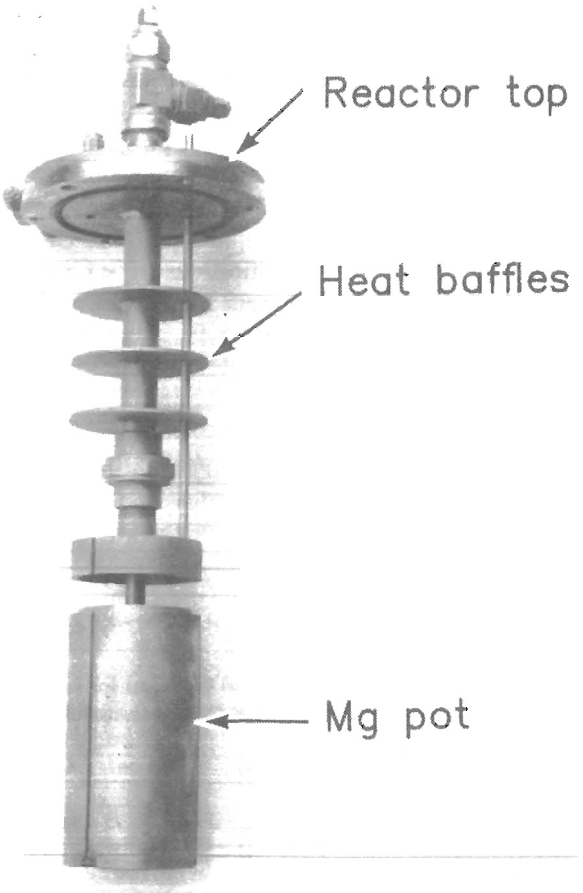

Figure 8.—Reactor top, heat baffles, and Mg pot.

temperatures. One of these thermocouples was placed between the two furnaces in the hottest zone of the reactor. The other was placed 13 in above the bottom of the lower furnace in a cooler part of the reaction zone.

$TiCl_4$ was vaporized before feeding into the reduction reactor top using the equipment shown in figure 9. UHP Ar was fed into the top heat-resistant glass cylinder, where it was heated to prevent condensing $TiCl_4$ vapor in the lower glass cylinder, the $TiCl_4$ vaporizer. The vaporized $TiCl_4$ was carried by the Ar into a heated 1/4-in tube and then into the reactor. This entire apparatus was maintained at 200° C and worked well in delivering vaporized $TiCl_4$ to the reaction zone.

A temperature profile of the reactor was determined and is shown in figure 10. To determine the profile, a stainless steel, sheathed thermocouple was lowered into the reactor at 3-in intervals, starting at 6 in below the furnace top. Argon was metered in at rates equal to those in a typical reduction run. The furnace temperature was controlled to maintain 1,000° C at the Mg pot thermocouple, the desired reading for a reduction run. The temperature was allowed to equilibrate for 2 h before taking measurements. Each temperature was recorded after it had stabilized for 15 min. Temperatures at the Mg pot and bottom reaction zone were similar to those measured with the probe. The temperature profile illustrates that no "reaction temperature" exists; rather, a reaction temperature range exists in the reaction zone.

In a typical reduction reaction, three powder products were formed—TiN, $MgCl_2$, and unreacted Mg. Some of the powder adhered to the reactor walls and baffles. The larger powder particles in the exiting gas stream fell into the receiver located immediately below the reactor. This

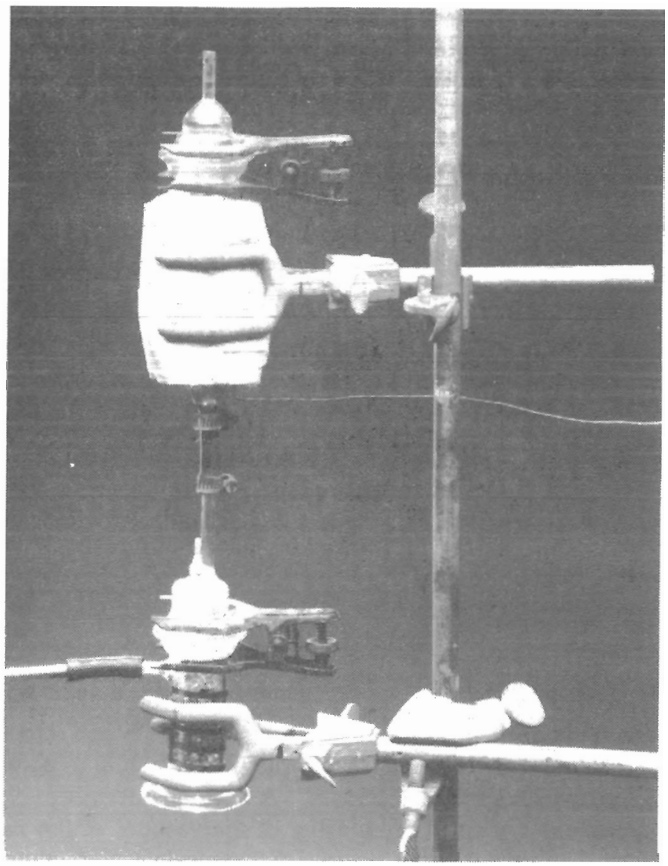

Figure 9.—Ar heater shown above $TiCl_4$ vaporizer.

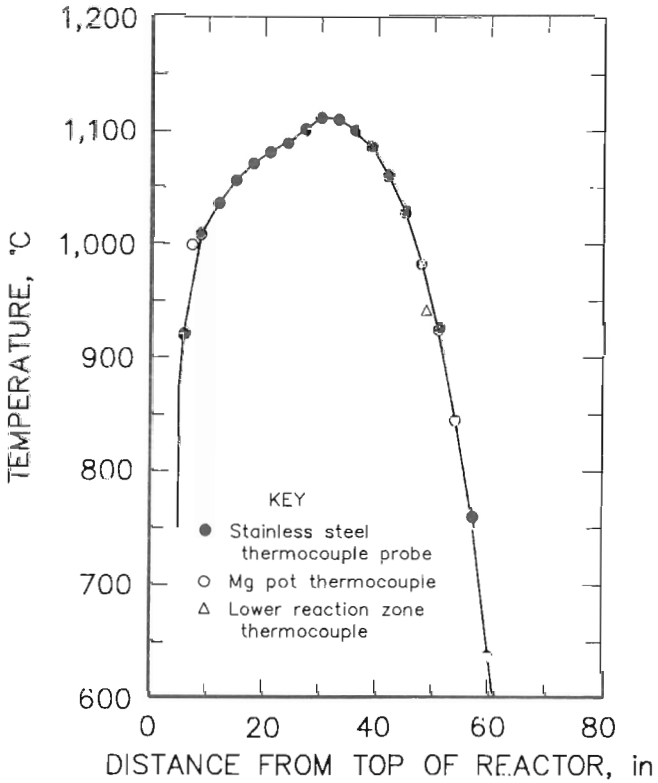

Figure 10.—Temperature profile of reduction reactor.

prevented plugging in the exit line. A ball valve located above the receiver isolated the receiver from the rest of the system. The bulk of the powder was carried through stainless steel and flexible plastic lines to the lower sidewall of the ESP (fig. 11), where it was separated from the gas stream (*16*).

The pipe-type ESP was 7-3/4 in ID, 18 in tall, and constructed of AISI Type 304 SS. A stainless steel funnel directed the powder into the glass receiver below the ESP. A glass or Micarta[6] laminated plastic top with an O-ring seal reduced arcing and prevented air contamination. A wire electrode with a Pb weight at the bottom was suspended from the center of the top and attached to a high-voltage power supply operated at 0.1 mA and 12 to 15 kV. The ESP was heated with band heaters and maintained at 160° C to prevent condensation of any unreacted $TiCl_4$ vapors.

Attached to the bottom of the ESP was a stainless steel ball valve used to isolate the powder in the ESP from the atmosphere below. The ball valve also allowed changing glass powder receivers during a run.

[6]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

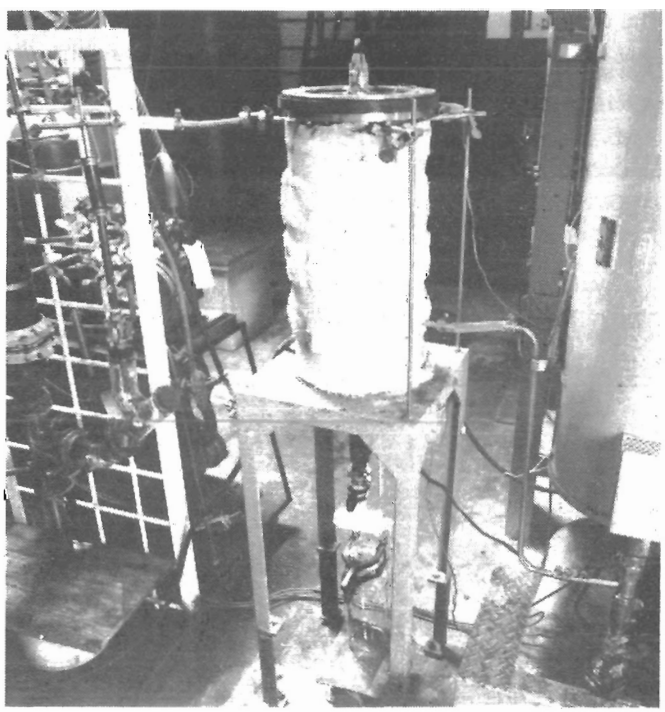

Figure 11.—Closeup of ESP showing connections and receivers.

The carrier gas and the unrecovered, suspended material exited the side of the ESP near the top and entered a packed-bed scrubber. The scrubber contained 5 wt pct HCl to remove residual $TiCl_4$ and powder products from the exiting gas stream. Also connected to the crossover line from the ESP to the scrubber was a vacuum line leading to a mechanical vacuum pump. This pump was used to evacuate the reactor and powder collection train, allowing backfilling with UHP Ar prior to reduction.

VACUUM DISTILLATION

The powder, as prepared in the reduction reaction step, included TiN, $MgCl_2$, and Mg. A process was needed to separate pure TiN from the other powders. Prior research proved the effectiveness of thermal vacuum distillation on purifying Ti and Zr sponge by removing the $MgCl_2$ and excess Mg (*17*). Since the TiN system was so similar to the Ti and Zr systems, thermal vacuum distillation was used for purification.

The distillation equipment (fig. 4) consisted of a retort, furnace, piping, and vacuum pumps. The retort was mounted vertically and contained a lower hot zone and a higher cool zone (shown schematically in figure 5). The 36-in-long hot zone section was of Type 310 SS, 4 in. in diameter, while the cool zone section was constructed of 24 in of Type 304 SS, 6-in pipe. Three inches above the hot-to-cool zone transition, a 17-in-long water jacket was welded around the 6-in pipe. The water jacket condensed the $MgCl_2$ and Mg vapors and prevented them from entering the pump system piping. The diameter of the cool zone was larger than the hot zone to prevent the condensable material in the system from reducing the inside pipe diameter. This aided in removing the crucible holding the TiN powder without dislodging $MgCl_2$ or Mg, which could have fallen into and contaminated the purified powder. Located in the center of the O-ring sealed top was a thermocouple well, which extended to just above the top of the loaded crucible. Attached to the thermocouple well were five 5-1/4-in-diameter stainless steel baffles, which provided additional cool surfaces and forced the evacuating gases to the outside wall. The top also supported a 5-3/4-in-diameter stainless steel shield, which aided in cleaning the retort by providing a removable cool surface on which the $MgCl_2$ and Mg could condense.

The distillation furnace had resistance-type heating elements and stood 36 in high. It supported the distillation retort and was supported by an external rack. The bottom of the furnace and retort rested on two layers of fire brick. Two thermocouples on the outside of the retort were used for temperature control. A digital temperature readout was produced from the thermocouple, which was inserted into the retort top thermocouple well.

The piping system consisted of 6 ft of 1-in galvanized pipe with vacuum valves on each end. These valves isolated the distillation retort or the piping system and retort. Prepurified Ar was plumbed to the piping system to backfill the retort when necessary. A vacuum thermocouple gauge tube allowed monitoring of the vacuum in the retort. The vacuum lines led to a mechanical vacuum pump, rated at 60 L/min, which was used as a roughing and backing pump. Valving could be changed to include a small, air-cooled, oil diffusion pump in the system. A vacuum thermocouple gauge tube and an ionization gauge monitored the vacuum ahead of the diffusion pump.

EXPERIMENTAL PROCEDURES

EQUIPMENT PREPARATION

Synthesis of TiN powder was accomplished by reacting anhydrous NH_3 or UHP N_2 with $TiCl_4$ in the presence of Mg. These reactions are listed below with the Gibbs energy (ΔG) listed at 1,200 K.

$$TiCl_4 + 2\ Mg + 0.5\ N_2 \rightarrow TiN + 2\ MgCl_2,$$

$$\Delta G = -126.95\ \text{kcal/mol}\ (18).$$

$$TiCl_4 + 2\ Mg + NH_3 \rightarrow TiN + 2\ MgCl_2 + 1.5\ H_2,$$

$$\Delta G = -147.27\ \text{kcal/mol}\ (19).$$

TiN formation was believed to occur by the simultaneous reaction of $TiCl_4$ and Mg and Ti and the nitrogen source as shown in the reactions below (*20*).

$$TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$$

and

$$Ti + 0.5\ N_2 \rightarrow TiN$$

or

$$Ti + NH_3 \rightarrow TiN + 3/2\ H_2.$$

Elger theorized that a TiN coating formed on the surface of the Ti particle, requiring the nitrogen to diffuse through the coating to react with the pure Ti inside the coating (*20*).

Harbuck (*14*) discovered that an optimum of 135 to 150 pct of stoichiometric Mg requirements was necessary to assure high conversions of $TiCl_4$ to TiN. The reactor design, in which the Mg pot was contained in the upper

reaction zone, prevented independent control of the Mg pot and reactor temperatures. Consequently, the Mg pot temperature, which primarily determined the rate of Mg vaporization, was dependent upon the reaction zone temperature, not the ideal temperature, for Mg vaporization. Therefore, Mg vapor amounts outside of the optimum range were often present during a reduction run.

The TiN powder should have a Ti-N ratio of 1:1 (22.6 wt pct nitrogen). This ratio was suggested by Alexander to achieve maximum wetting of the TiN powder by Ni during the compact sintering step.[7] All reported nitrogen values were determined by the Kjeldahl method, as reported by Bollman (*21*). The Kjeldahl method involves heating the nitride in tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and phosphoric acid (H_3PO_4) until gas evolution nearly stops. Water is then added and the mixture is distilled and titrated (*22*). This was believed to be the best method of determining nitrogen at the 20+-wt-pct level without an accurate standard.

The procedures used prior to reduction centered on producing a clean system, good reactant contact, and efficient powder collection. After a reduction run, the reactor was washed with water and wire brushed to remove most of the residual powder. It was then wiped with a clean cloth, heated to 300° C for 4 h, and left at 100° C with a watch glass on top to prevent debris from falling in.

Before beginning a reduction run, the pure Ti reactor baffles (fig. 7) and the Mg pot with baffles (fig. 8) were sandblasted to remove impurities. The reactor baffles were placed in the reactor, after which the pickled and dried Mg rods were loaded into the Mg pot. The Mg pot with rods were weighed and attached to the reactor top.

The reactor top and Mg pot assembly were bolted into position, and water lines were attached to the top flange to cool the O-ring. After purging all lines with Ar, the lines were connected to the appropriate fittings on the reactor top. UHP Ar was fed into the Mg pot to reduce oxidation of the Mg rods in the reactor, while prepurified Ar purged the equipment during and after assembly. All assembled equipment was pressurized overnight to exclude air.

All stainless steel lines and valves and glass parts were washed, rinsed, and dried in an oven after each run. They were then ready for assembly when needed. The stainless steel tube leading from the reactor bottom to the inlet of the ESP was connected with new, flexible plastic lines. Heating the ESP to 100° C after cleanup kept it dry, and installing the top with an O-ring prevented air infiltration. The first ESP receiver (ESP1) was installed prior to evacuation and backfilling. The outlet of the ESP was attached to a stainless steel cross, which led to the scrubber inlet, scrubber bypass (to an exhaust hood), and vacuum pump. The vacuum pump evacuated the reactor and collection train before beginning the reaction.

After assembling the equipment as described above, the $TiCl_4$ vaporization equipment was installed using Viton fluorelastomer tubing as couplings. The entire system was then pressure checked to approximately 4 psig. An arbitrary leak rate of 0.002 psig/min was set as the maximum allowed to run. Given an acceptable leak rate, the entire vaporizer, reactor, and collection train were evacuated for at least 1/2 h and backfilled with prepurified Ar. The reactor temperature was raised to 300° C and the ESP to 150° C during this time. The reduction run was started if the O_2 level was <0.1 ppm after 5 min as measured at the vacuum pump. If the O_2 level was not <0.1 ppm, the system was evacuated, backfilled, and measured again. No runs began unless the O_2 was <0.1 ppm.

REDUCTION REACTION

Reduction runs began by increasing the temperature to 850° C at the top of the Mg pot and 160° C in the ESP. The latter temperature prevented unreacted $TiCl_4$ fumes from condensing in the ESP. Prepurified Ar, admitted through the top of the reactor, purged the system during heating. Distilled $TiCl_4$ was poured into a 1,000-mL graduated cylinder filled with Ar. Tubing from the graduate ran through a peristaltic pump to the $TiCl_4$ vaporizer, which was heated to 200° C or higher.

When the Mg pot temperature reached 850° C, UHP Ar flows to the Mg pot and $TiCl_4$ vaporizer were adjusted. NH_3 and $TiCl_4$ flows were started at one-half and one-fifth the target feed rates, respectively. The high-voltage power supply and acid scrubber were started, and prepurified Ar flow to the reactor top was stopped. Upon reaching 950° C at the Mg pot, all flows were increased to those desired for the run. $TiCl_4$ levels in the graduate, needed to determine flow, and all thermocouple temperatures were recorded at 15-min intervals. ESP1 was changed after 15 min, since this would remove powder containing impurities caused by startup. Most runs lasted 2 to 2-1/2 h at a temperature of 950° C or greater in the Mg pot. After the reduction run was completed, the glass stopcock above the second ESP receiver (ESP2) was adjusted to prevent air infiltration and powder contamination during transfer to the glove box. The residual powder and reaction equipment was handled as previously described.

VACUUM DISTILLATION

Vacuum distillation began by loading the crucible containing the powder from ESP2 into the distillation retort and bolting the top into place. The roughing pump then evacuated the system overnight.

[7]Work cited in footnote 4.

After reaching a pressure of 25 μm Hg or less, initial heating to 200° C commenced. The set point was then increased in 50° C increments, provided the pressure remained below 100 μm Hg. Heating proceeded slowly to avoid rapidly volatilizing the $MgCl_2$ and Mg, which could contain entrapped TiN powder, since carryover of TiN powder into the gas stream would reduce the purified powder yield. Vaporized $MgCl_2$ and Mg condensed in the upper, cool section of the retort on the wall of the water jacket. After reaching the target distillation temperature of 875° C, the diffusion pump was added to the system. The powder was distilled for 24 h at 875° C, after which the retort cooled with the diffusion pump running for several hours before being switched off. The roughing pump evacuated the retort until it was opened for powder transfer to the glove box. All equipment was thoroughly washed and dried before the retort was closed for heating and evacuating overnight. A ball valve was then closed to isolate the retort until the next distillation run. The heating procedure was done to eliminate as much contamination as possible from residuals left in the retort.

LEACHING AND DRYING

Crude powder collected in the receiver below the reactor, the ESP1, the scrubber acid, and all connecting lines were analyzed for a material balance. This powder was acidified with 10 wt pct HCl and stirred for 24 h to dissolve Mg and $MgCl_2$. Only TiN (with undissolved impurities) was left in the solid phase. The solids were separated from the liquid using a pressure filter and rinsed with distilled water. Rinsing continued until no precipitate formed with silver nitrate ($AgNO_3$), which indicated low levels of chlorides. The filter cake was dried at 100° C overnight, weighed, split, and sampled. The filtrate was also sampled. Samples were used for Ti mass balances.

POWDER HANDLING

Care was exercised in handling all powders to ensure isolation from air to minimize O_2 and moisture pickup, which could lead to contamination. Therefore, the powders were exposed only to an atmosphere of <0.1 ppm O_2 in a vacuum glove box, which was monitored by an O_2 analyzer. All sampling, transfers, and storage were performed in the glove box.

The powder to be vacuum distilled, containing TiN, $MgCl_2$, and Mg, was collected only in the ESP. This powder fell to the bottom of the ESP, through the stainless steel ball valve, and into the heat-resistant glass receiver (fig. 11). A small receiver was in place during heating and the first 15 min of the reduction run. After closing the stainless steel ball valve, another larger glass receiver was installed in place of the first. The new receiver and attached glassware were heated in a 50° C oven overnight and purged with prepurified Ar before use. This receiver top had a ground-glass stopcock, which was closed after the run to exclude air from contacting the powders during transfer to the glove box. After connecting the new receiver to the ESP at the ground-glass joint, the receiver and adjacent piping were evacuated for 2 min and backfilled with prepurified Ar. The evacuation and backfilling procedures were repeated two more times before the ball valve was opened to let the powders fall into the receiver. This was done to remove as much air and moisture as possible before exposing the ESP receiver to the powder.

After completion of the reduction run, the receiver containing the powder was placed inside the glove box antechamber and evacuated overnight. The leak rate of the antechamber was measured. The receiver was not placed inside the glove box unless the leak rate was <1 μm Hg/min and the atmosphere in the glove box was <0.1 ppm O_2. Prepurified or UHP Ar was used to backfill the glove box main chamber, and crude powder from ESP1 was used as an oxygen getter. Another critical step for decreasing impurity levels was to backfill the antechamber with prepurified Ar after each use to prevent air infiltration into the main chamber. All powder transferring and sampling was accomplished inside the glove box.

The above procedures were followed whenever powder was loaded into, unloaded from, or handled in the glove box. However, upon loading and unloading the distillation retort, an additional precaution was employed. The crucible used to distill the powder had a cover with holes to allow the volatiles to escape during distillation. These holes would allow air contact with the powder during transfer to and from the glove box. While in the glove box, the crucible and powder were placed inside a sealable plastic bag to protect them from contact with air during transfer. The bag was opened near the distillation retort, and the crucible containing the crude powder was placed inside the retort filled with prepurified Ar. Therefore, powder contact with air was minimized, but not eliminated. Upon removal of the crucible containing distilled powder, the same plastic bag was filled with prepurified Ar immediately before placing the crucible in it. The bag and its contents were then placed inside the antechamber, which was immediately evacuated. The previously described procedures were then followed to handle the powder.

PARTICLE SIZE ANALYSIS

Particle size analysis was performed on an instrument using gravitational or centrifugal sedimentation. Samples were lightly ground, stirred in 25 mL of deionized water with a dispersing agent, and dispersed for 1 min using an ultrasonic probe. Several drops of the solution were

transferred to 25 mL of deionized water and dispersed for 10 s with the ultrasonic probe before measurement. The dispersion medium viscosity and density and the powder density, as measured using a stereopycnometer, were entered into the instrument. The instrument was calibrated using the dispersion medium without powder as a reference. Three aliquots of the dilute mixture were measured for particle size, and the median and standard deviation for each measurement were recorded and averaged. Therefore, the reported median and standard deviations are a mean of three measurements. Powders were measured from each of the sample locations for each reduction run. The particle size analysis was repeated on a second sample taken from one of the locations to confirm the consistency of the results.

A transmission electron microscope (TEM) was used to check the particle sizes measured by the particle size analyzer. The samples were prepared by dispersing the powder in ethylene dichloride containing a dispersing agent. The mixtures were stirred and dispersed by an ultrasonic processor before being formed into thin films and mounted on microscope grids. Particle sizes were measured using an image analyzer and photographic prints.

RESULTS AND DISCUSSION

Optimally, TiN powder contains 22.6 wt pct nitrogen and 77.4 wt pct Ti. Experiments were completed to determine the effects of various parameters on the nitrogen content of the TiN powder. However, oxygen and other impurities were found in the final product. The sources of these impurities were the reactants, the materials of construction, and air. Methods to reduce contamination in the distilled TiN powder were studied, as was the particle size of the powder at various locations in the collection train. The distilled TiN powder as a component of TiAlON was physically evaluated.

TiN PRODUCTION PARAMETERS

Reduction reaction parameters were changed to study their effect on TiN powder. Although the nitrogen content in the distilled TiN powder was the most critical analysis, particle size was also examined and is discussed in the "Particle Size Analysis" section. The nitrogen content in TiN powder was analyzed on a weight percent basis with the optimum amount being stoichiometric. Parameters were studied in the small reactor, results of which have been reported earlier (*20*), and also in this large reactor. When possible, experiments were run, varying only one parameter at a time so that results could be directly compared with previous and succeeding runs. Liquid $TiCl_4$ was fed to the reactor, except when studying the feed state or when noted in the text. However, the involved procedure increased the opportunity for statistical variation and complicated direct comparisons.

The effects of the following parameters were evaluated:

1. Reaction temperature,
2. Reductant quantity,
3. Nitrogen source,
4. NH_3 feed rate,
5. $TiCl_4$ feed rate,
6. Reaction zone baffles,
7. Residence time, and
8. $TiCl_4$ feed state.

Reaction Temperature

Thermodynamically, the synthesis of TiN from $TiCl_4$, Mg, and NH_3 is more favorable at 1,000 K than at 1,400 K (*19*).

$$TiCl_4 + 2\ Mg + NH_3 \rightarrow TiN + 2\ MgCl_2 + 1.5\ H_2,$$

$$\Delta G_{1,000\ K} \rightarrow -151.36\ kcal/mol,$$

$$\Delta G_{1,400\ K} \rightarrow -141.91\ kcal/mol.$$

Since the products are favored and stoichiometric TiN is desired, the effect of changing the reaction temperature was measured by analyzing the TiN for nitrogen.

However, the effect of the reaction temperature on the amount of nitrogen in the TiN powder was not well defined. Since the reductant container (Mg pot) was located in the upper reaction zone, the temperature effects on the Mg pot and reaction zone could not be separated completely. Higher temperatures increased the Mg vaporization and reaction temperature simultaneously. However, it was not known if the increased reductant or the increased reaction temperature caused the change in nitrogen content. A design in which the reductant was pumped into the reactor as a gas would be superior to the present design. The independent study of these parameters could then be accomplished.

Upper reaction zone temperatures were measured 7 in below the bottom of the Mg pot. They ranged from 1,080° to 1,150° C because the corresponding amounts of Mg vaporized were less than stoichiometric for the lower temperature and greater than three times stoichiometric

for the higher temperature. In addition, the materials used for the reactor also limited the highest temperature. The temperature range produced distilled TiN powder that showed no change in the nitrogen content. Consequently, within the narrow range tested, the reaction temperature did not affect the powder quality.

Reductant Quantity

The amount of Mg vaporized during a reduction reaction run was critical because it was the primary reductant for $TiCl_4$. Stoichiometrically, 2 mol of Mg were necessary to reduce 1 mol of $TiCl_4$. Less Mg left unreacted $TiCl_4$, while excess Mg drove the reaction toward the products. However, excess reductant increased the load on the distillation system and potentially left more Mg as an impurity in the product. This impurity problem will be discussed in the "Impurity Reduction" section.

Adjusting the temperature of the Mg pot was the primary method of controlling the amount of vaporized Mg. The amount of Mg vaporized was directly related to the amount available for reaction with $TiCl_4$ and NH_3. Figure 12 shows an increase in nitrogen content in the distilled TiN powder with an increase in the Mg vaporized (in moles). However, above 6 mol of Mg, the nitrogen content leveled out or dropped slightly. Increased amounts of Mg reduced more $TiCl_4$ to Ti, which increased the concentration of Ti available to react with NH_3. Therefore, more TiN was produced and the nitrogen content in the final distilled TiN powder was increased. Unfortunately, more vaporized Mg resulted in more Mg impurities in the TiN product.

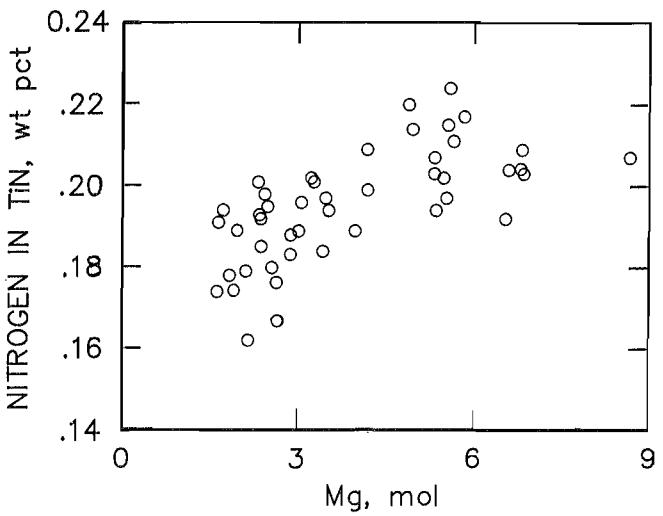

Figure 12.—Effect of amount of Mg on concentration of nitrogen in TiN.

Nitrogen Source

To produce TiN powder in a vapor-phase reaction, a source of nitrogen must be available to bond with the Ti. The two most common nitriding agents are N_2 and NH_3. The vapor-phase reactions with $TiCl_4$ were shown in the "Equipment Preparation" section and indicate that NH_3 is the favored nitride source. Thermodynamically, the reaction of Ti with nitrogen is favored over Ti with H_2 (*19*).

$$Ti + H_2 \rightarrow TiH_2 \quad \Delta G_{1,200\ K} = 5.09 \text{ kcal/mol.}$$

$$Ti + N \rightarrow TiN \quad \Delta G_{1,200\ K} = -53.76 \text{ kcal/mol.}$$

Therefore, the NH_3 reaction to produce TiN is preferred.

The effectiveness of the nitriding agent was measured by comparing the amounts of nitrogen in the distilled TiN powder. Tests were run in the smaller reactor and reported by Elger (*20*). These tests showed higher average nitrogen contents in the distilled TiN when using NH_3. Also, much lower stoichiometric amounts of nitrogen were needed to produce the same nitrogen content in TiN when using NH_3 rather than N_2. These experiments were repeated in the large-scale reactor with similar results. Therefore, NH_3 was a much more effective nitriding agent than N_2.

NH_3 Feed Rate

Using NH_3 as the nitrogen source, the effect of varying the feed rate was considered. The rate was measured stoichiometrically based on the $TiCl_4$ feed rate. A higher flow of NH_3 gas would increase the nitrogen concentration in the reactor, which would increase the number of desired atomic collisions and possibly increase the nitrogen content in the distilled TiN. However, the increased NH_3 flow rate would also decrease the residence time, which could decrease the amount of nitrogen in the distilled TiN. Several flow rates were investigated based on the feed rate of $TiCl_4$ and the stoichiometric amount of NH_3 needed to reduce it. Flow rates were reported in multiples of the stoichiometric amount of NH_3.

The flow rate of $TiCl_4$ was determined by the amount of $TiCl_4$ pumped during the time the reactor was at the reaction temperature. The NH_3 flow rate was controlled by a flowmeter and was held constant throughout the test.

Targeted NH_3 feed rates were 3, 5, 7.5, and 12 times stoichiometric. All rates were greater than that targeted because the $TiCl_4$ flow rate was increased gradually during startup, which decreased the total $TiCl_4$ fed to the reactor.

The final stoichiometric NH_3 flow rate increased as a result of the variation in $TiCl_4$ flow rate.

Runs feeding 12 times stoichiometric NH_3 caused severe operational problems. Although numerous attempts were made, no run succeeded in producing enough powder to distill.

Table 2 shows that over the range of NH_3 flow rates from 3.3 to 12.4 times stoichiometric, no trends in the nitrogen content in TiN powder were apparent. Therefore, five times stoichiometric NH_3 was used to conserve reactants.

Table 2.—Effect of changing NH_3 feed rate on nitrogen content of distilled TiN powder

NH_3, times stoichiometric	Run	Nitrogen in leached TiN powder from reactor receiver, wt pct	Nitrogen in distilled TiN powder, wt pct
3.3	44	19.0	20.4
3.4	43	19.4	20.7
5.5	49	19.2	20.9
8.0	40	19.6	21.1
8.1	41	20.0	20.2
8.2	39	20.2	20.1
12.4	45	19.4	[1]

[1]Not enough powder was collected to distill, so no sample was analyzed.

$TiCl_4$ Feed Rate

$TiCl_4$ is the source of Ti in the reduction reactor. Its flow rate dictates the amount of NH_3 and Mg needed for the reaction and might affect the nitrogen content in the distilled TiN powder. High flow rates increase the $TiCl_4$ concentration in the reaction zone, which could increase the nitrogen content in the distilled TiN powder. However, if $TiCl_4$ is fed as a liquid, a higher flow rate could decrease the amount vaporized and cause the opposite effect, as could increased flow rates, which reduce residence times.

A series of tests was run in which the target $TiCl_4$ feed rate was either 1.4 or 2.8 mL/min. $TiCl_4$ was fed as a liquid with and without reactor baffles. Attempts were made to hold other parameters constant. However, complications again arose in keeping reaction temperatures and the amount of excess Mg constant. When reducing the $TiCl_4$ flow rate, the Mg vaporization rate was also reduced to maintain a constant excess of Mg. To decrease the amount of Mg vaporized, the temperature was decreased, which reduced the reaction temperature. Therefore, reducing the $TiCl_4$ feed rate could not be accomplished completely independent of other parameters.

Table 3 shows the nitrogen content in the distilled TiN at two different $TiCl_4$ feed rates. Other pertinent parameters that affect nitrogen content are also shown. The mean nitrogen content is 19.9 wt pct for the lower feed rate and 18.9 wt pct for the higher feed rate. Although the mean differences are not statistically significant, further study would be beneficial if Mg could be vaporized outside of the reactor and fed to the reaction zone as a vapor.

Table 3.—Effect of $TiCl_4$ flow on nitrogen content of distilled TiN powder

$TiCl_4$ flow, mL/min	Run	Nitrogen content in distilled TiN, wt pct	Mg, times stoichiometric	Average Mg pot temp, °C
Without baffles:				
1.33	2	20.7	8.66	1,005
1.39	1	19.8	2.44	1,000
2.54	7	18.3	2.88	1,033
2.58	10	19.2	6.53	1,049
With baffles:				
1.41	6	18.4	3.43	1,002
1.41	13	20.3	6.85	1,001
1.43	9	20.3	5.33	1,000
2.50	8	19.4	5.35	1,031
2.59	16	18.8	2.89	998
2.65	15	18.9	3.02	1,000

Reaction Zone Baffles

Three diagonal baffles were mounted on a frame and placed inside the reactor immediately below the $TiCl_4$ feed tube (fig. 7). Holes allowed gases and powder particles to pass through. The baffles and frame were pure Ti instead of stainless steel to prevent Fe contamination of the powder. The baffles were used to mix the reactants, which improved vapor-phase contact and the possibility of a successful reaction. However, they increased the amount of powder trapped in the reactor and decreased recovery. Replacement was required when the baffles became embrittled and warped after 10 to 12 runs. Perhaps feeding gases at right angles would provide mixing and eliminate the baffles. Tests on feeding liquid and vaporized $TiCl_4$ to the reactor were completed.

Table 4 shows the effect of baffles on the nitrogen content in the distilled TiN powder. Although baffles were not necessary for mixing, the results indicate that mixing the reactants enhanced the nitrogen content.

Table 4.—Effect of baffles on nitrogen content of distilled TiN powder

Baffles	Run	Nitrogen in distilled TiN powder, wt pct
No	41	20.2
	49	20.9
	52	20.4
	53	21.4
Yes	57	21.4
	51	22.0
	50	22.4

Residence Time

The time spent by gases in the reaction vessel (known as residence time) could affect the chemical content and size of the final powder particles. A long residence time allows more time for successful vapor-phase collisions to occur and for mass transfer of nitrogen into the Ti particle. Increased nitrogen content in the TiN powder particles should result. However, prolonged time in the hot zone allows more particle collisions and sites for vapor-particle reactions, resulting in an increase in particle size.

Ideally, the time spent by each molecule in the reactor should be known, but the mixing, reactions, and changing density make this approach impractical (*23*). Therefore, the mean residence time for this research was determined using the following equation:

$$t = V/v,$$

where t = mean residence time, min,

V = volume, L,

and v = volumetric flow, L/min (*23-24*).

The volume in the equation above refers to the volume where reaction can occur—the reaction zone. The top of this zone was the bottom of the Mg pot because that was where the reactants were first contacted. The lower end of the reaction zone was harder to define and did not involve a definite boundary. A reaction temperature limit of 850° C was used to define the lowest extent of the reaction zone because little reaction was observed below this temperature. A reaction zone height of 104.7 cm and a volume of 8.06 L resulted.

The volumetric flow consisted of the sum of the incoming gas stream flows. Together with the volume as determined above, the residence time was calculated. The Ar to the $TiCl_4$ line, Ar to the Mg pot, $TiCl_4$, and NH_3 or N_2 are the regulated flow constituents. The Mg reactant could not be regulated with any certainty. No attempt was made to precisely control its flow, but it was included in the mean residence time calculation.

Values of mean residence time ranged from 0.53 to 0.90 min, based on the reactant flows. Figure 13 shows the nitrogen content of the TiN powder at the different mean residence times. Since the data are scattered, the nitrogen content in the TiN powder is not affected by mean residence times between 0.53 and 0.90 min. One explanation is that the reaction kinetics are very rapid and residence times beyond 0.5 min are not needed to increase the nitrogen content in the TiN powder.

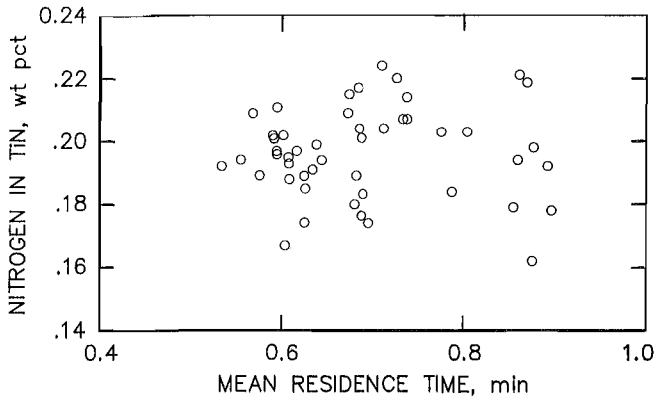

Figure 13.—Effect of mean residence time on concentration of nitrogen in TiN.

$TiCl_4$ Feed State

Completely vaporized reactants are important to produce a vapor-phase reaction. The Mg was vaporized inside the reactor and transported in a gaseous stream. The NH_3 was fed as a gas. Therefore, the $TiCl_4$ also must be fed as a gas, although it initially was fed as a liquid into the hot reactor. Since this did not ensure completely vaporized $TiCl_4$, the external vaporizer was used.

A true vapor-phase reaction should produce several advantages: a smaller particle, no mass transfer into a solid particle is needed to produce homogeneous TiN, and higher nitrogen contents (stoichiometric) are possible because mass transfer is not a problem.

Two effects of feeding vaporized, instead of liquid, $TiCl_4$ were studied—particle size and nitrogen content in the distilled TiN. With a vapor-phase reaction, all collisions are between separate molecules, so a smaller particle is expected. Limited particle growth is anticipated since TiN is relatively unreactive. A partly liquid reaction should result in larger particles because small drops of $TiCl_4$ react. Table 5 shows the effects on particle size of $TiCl_4$ vaporization before introduction into the reactor. No difference in the particle size is apparent from the data.

The nitrogen content in the distilled TiN was also expected to increase when the $TiCl_4$ was vaporized prior to introduction into the reactor. A vapor-phase reaction should allow more intimate contact of the reactants and eliminate the need for mass transfer into the particle to completely nitride the Ti. Therefore, more of the Ti is nitrided and a ratio closer to 1:1 (Ti to nitrogen) should result. Of all the parameters changed, this one made the largest increase in nitrogen content (table 5). Consequently, a complete vapor-phase reaction is needed to maximize the nitrogen content in TiN.

Table 5.—Effect of $TiCl_4$ vaporization on particle size and nitrogen content of TiN powder

$TiCl_4$ vaporization	Run	Nitrogen content in distilled TiN, wt pct	Distilled TiN powder median diam, μm	ESP1 TiN powder median diam, μm
No	39	20.1	0.15	0.11
	41	20.2	.12	.12
	49	20.9	.10	.10
Yes	54	20.7	.13	.12
	57	21.5	.10	.08
	58	21.6	.12	.08
	51	22.0	.12	.10
	50	22.4	.16	.10

IMPURITY REDUCTION

In addition to stoichiometric nitrogen content in the TiN powder product, the lowest possible impurity levels are desired. Although no standards are available, specifications have been published. Yamamoto lists the following impurities: O_2, <1.0 wt pct; Fe, <1.5 wt pct; Cr, <0.5 wt pct; and traces of Na, Ca, Si, S, Cu, Mg, P, B, etc. (*8*). Data sheets from Hermann C. Starck, Inc., list the following specifications for TiN: Ti, ≥77 wt pct; N, ≥20.0 wt pct; C, ≤0.1 wt pct; O, ≤2.0 wt pct; and metallic impurities, total of ≤0.15 wt pct. Alexander has reported that a higher nitrogen content and a lower oxygen content than those listed above are imperative for the optimum wetting needed to produce a dense compact.[8] Therefore, a powder is desired with high Ti and nitrogen contents and low impurities.

The contaminants of the TiN formed in the vapor-phase reaction can be separated into three groups—metals, reaction products, and gases. The metal impurities result from the materials used for the reactor and reactant delivery system and from impurities in the reactants. The reaction product impurities are a result of the reduction reaction between $TiCl_4$ and Mg. These are $MgCl_2$ and unreacted Mg. The gaseous impurities come from the air and contained or contacted compounds. These impurities are mainly oxygen and C. Carbon was low and not a problem in the distilled powder. The various sources of the impurities require different methods to reduce or eliminate them.

Metallic Impurities

One possible source of metallic impurities is from the materials used for the lines, containers, and reactor. Temperature, chemicals, and moving powder particles cause corrosion and erosion of the materials used in the reaction and distillation systems. These materials report to the powder product and are difficult to remove.

[8]Work cited in footnote 4.

Since stainless steel is a common material that is relatively cheap, easily worked, and can withstand high temperatures, it was used for the reactor, Mg pot, delivery tubes, baffles, and retort. However, early analyses indicated high Fe and Cr levels in the distilled TiN powder. Replacing the stainless steel $TiCl_4$ feed tube with an Al_2O_3 tube and the stainless steel Mg pot with a pure Ti pot reduced the average Fe content in the distilled TiN powder from 3.0 to 0.20 wt pct. The Cr content of the TiN powder was also reduced from 1.18 to 0.15 wt pct. The Fe impurity in the $TiCl_4$ feed accounted for 0.02 wt pct Fe in the TiN product. This was the base Fe level, since it was difficult to purify the $TiCl_4$ further.

The use of Al_2O_3 as the $TiCl_4$ feed tube introduced the possibility of increased Al and oxygen contamination. Inspection of the feed tube after each reduction run showed no visual degradation. Chemical analyses of the distilled TiN before and after using the Al_2O_3 feed tube averaged 0.05 and 0.12 wt pct Al, respectively. Therefore, the use of Al_2O_3 drastically reduced Fe and Cr contamination, but slightly increased Al impurities. Proposals to line the reduction reactor with Al_2O_3 to further reduce Fe contamination must be balanced by the possible increase in Al impurities.

Other materials were also used for the $TiCl_4$ feed tube, but proved unsatisfactory. Titanium and titanium alloy tubing disintegrated at its lower end—the part in the Mg pot and reaction zone. Quartz tubing disintegrated in the Mg pot, reducing the run time. Nickel-based alloys proved disastrous because the Mg vapor in the Mg pot dissolved the Ni in the feed tube. The result was a plugged feed line when the Mg vapor reduced $TiCl_4$ in the feed line. Therefore, the Al_2O_3 tube proved the most satisfactory by withstanding the harsh environment better than other materials, which allowed its use for multiple runs.

Mg and Cl Impurities

The powder collected in ESP2 contained the TiN powder targeted for further use in sintered shapes. Thermal vacuum distillation of Ti sponge is the best method of purification (*17*). Therefore, thermal vacuum distillation was chosen to remove the Mg and $MgCl_2$ impurities from the TiN powder. A low level of oxygen resulted, but the Mg and Cl levels were higher than for acid collection.

The Mg and Cl levels in the distilled TiN powder remained too high and varied from run to run. The average Mg content for 47 distillations was 0.64 wt pct with a high of 2.7 wt pct and a low of 0.025 wt pct. Attempts to improve the distillation effectiveness centered on increasing the time and temperature. The temperature increase was limited to 875° C because higher temperatures caused hard chunks of TiN powder to form, which made grinding more difficult. Heating times were increased from 10 to 30 h.

These attempts appeared somewhat successful at first, but slowly the Mg and Cl levels rose to near previous ones.

Since lower Mg and Cl contents are needed for high-quality TiN powder, several suggestions to increase the distillation effectiveness have been proposed. With a 10-in-deep bed of powder, not all of the Mg and Cl can readily escape to a cool surface for condensation. Perhaps a better system would rotate the powder to drop it through the atmosphere in the retort, such as in a diagonal screw feeder. This would free all particles and allow separation of $MgCl_2$ and Mg from the TiN. A bleed stream of Ar might aid in the desired separation. More efficient pumping with a larger capacity system and a higher ultimate vacuum should also aid purification.

Oxygen Impurity

Oxygen, as an impurity in TiN, causes inferior sintered specimens with microporosity, embrittlement, and cracking. Since no industrial, standard specifications exist for oxygen in the TiN powder, the lowest possible concentration is desired. However, reducing the oxygen content is difficult because it is found in the air and reactants and on material surfaces. For these reasons, extreme care must be taken in all phases of producing and handling the powder. As operating experience was gained and greater care was taken, a consistently lower oxygen content appeared in the TiN product.

All reactants and gases must be as pure as possible to reduce contamination of the reactor, collection train, and powder. Except for the anhydrous NH_3, all reactants were purified and handled to minimize the oxygen content. A purer grade of NH_3 should be used, since the reaction was the most critical step in allowing oxygen to enter the TiN powder particles. The equipment received a thorough cleaning, drying, and bake out to reduce O_2 and moisture contents before assembly. Prior to the reduction reaction, the reactor, ESP, and all connecting lines were heated and evacuated to drive O_2 and water molecules off the walls. Only UHP Ar was used as a carrier gas during the reaction.

Powder handling was thought to add chiefly to oxygen contamination on the powder surface. Whenever possible, the powder was handled under purified Ar cover or in an atmosphere measured to contain <0.1 ppm O_2. The one exception was in transferring the powder from the glove box to the distillation retort and back, during which the powder was protected in an Ar-filled plastic bag. However, the powder-containing crucible was exposed to air briefly while loading and unloading the retort. Although the crucible had a lid and contained pure Ar, the transfer process still exposed it to room air. In an improved design, the distillation retort would be directly attached to the glove box.

An increase in the TiN powder oxygen content from the Al_2O_3 tube was hard to determine because many oxygen sources contribute to the final impurity in the product and variations exist even for identical runs. However, the average oxygen impurity content dropped from 0.88 to 0.76 wt pct after using the Al_2O_3 feed tube. Therefore, the Al_2O_3 tube did not appear to adversely affect the oxygen content in the TiN powder product.

The precautions taken in using pure reactants and carrier gases, careful setup and operating procedures, and attentive powder handling techniques reduced the average oxygen content from 1.0 to 0.58 wt pct for the last nine reduction runs. Improvements are needed to lower the oxygen content of the TiN powder further, since even lower levels appear desirable for sintering.

Ti MATERIAL BALANCE

A Ti material balance of the reduction reactor and collection train was calculated for each reduction run. $TiCl_4$ flowed into the system as it was pumped into the reactor and out through the scrubber. Accumulations were present in the reactor, ESP, connecting lines, reactor receiver, ESP receivers, and scrubber. The only usable Ti was as TiN in ESP2. The rest of the accumulated TiN was unusable because of higher contamination levels.

Titanium recovery averaged 94 wt pct of the incoming Ti—essentially in the form of TiN. The unaccounted Ti either exited out the scrubber or accumulated in the reactor and train, but was unrecovered. Titanium in the usable TiN form averaged 46 wt pct of the incoming Ti.

Much of the unusable TiN was trapped on the baffles and walls of the reactor and collected during the first 15 min in the ESP. These two locations averaged over 75 wt pct of the unusable TiN. A longer running time could reduce the relative amount of TiN powder lodged on the baffles and reactor walls and discarded from the ESP. Therefore, the percentage of usable TiN recovered would increase with the length of the reduction run.

PARTICLE SIZE ANALYSIS

The particle size of the distilled TiN is very important, since a smaller particle produces a more uniform chemical composition, a superior product, and a part closer to the final size. However, smaller particles are also more reactive and therefore more susceptible to contamination, particularly by O_2 from the air. Determining the effect of parameters on particle size might help control the size produced in the vapor-phase reaction. The range of particle sizes produced during the reaction and where they accumulate in the system might also aid in collecting the desired powder sizes.

A particle size distribution analyzer, based on the principle of liquid-phase photosedimentation utilizing Stokes' sedimentation law, determined particle size. Stokes' law states that spherical particles settle by gravity at different rates through a liquid, depending on the diameter and density of the particle and the density and viscosity of the liquid. Powder samples were taken from the reactor and ESP, reactor receiver, ESP1, scrubber, and distilled powder. Examination of the powder was also done with a TEM to verify the particle size as measured on the particle size analyzer.

The TEM and particle size analyzer results are listed in table 6. The particle sizes determined by the TEM involved measuring micrographs with a magnification of 25,000, utilizing an image-processing system and video camera. The number of particles measured for each sample is listed in the table.

The TEM results are very consistent with particle size analyzer measurements taken from different reduction runs and different sampling sites in the powder collection train. The minimum size of 0.04 μm was the lower limit of the equipment and measuring technique. In fact, a few smaller particles were observed, but could not be accurately measured. No particle size over 0.31 μm was measured. Therefore, the particles were consistently small.

A statistical difference was noted in the particle sizes measured with the TEM and the particle size analyzer for the distilled and scrubber samples of run 56. Although mean particle diameters were compared to median particle diameters, these results differed by a factor of about 1.5. Being a direct measurement, the TEM particle size assured that two agglomerated particles were not measured as one, which could have happened using the particle size analyzer. Therefore, the TEM measurements gave a better indication of the particle size than the particle size analyzer, even though the population size was smaller. Improper dispersal of the particles would explain those instances in which the median diameter was larger than the mean diameter.

The other samples measured by both the TEM and the particle size analyzer listed in table 6 resulted in close agreement. However, TEM measurements were very time consuming, performed on a small population, and resulted in only a slightly smaller size than the particle size analyzer measurements. Therefore, the latter method was chosen to analyze the particles. One must remember that the particle size analyzer gave results slightly larger than the actual particle diameters because of incomplete dispersion. Therefore, the measurements reflect the upper limit of the particle size.

The TEM photomicrographs of the leached powder reveal particles similar in size and appearance (fig. 14). Notice that three distinct particle sizes are present, with the smaller and medium sizes being the most numerous. The shapes of the particles are distinctly crystalline, with many of the larger ones appearing cubical. This reflects ordered powder formation in the vapor phase. Most distilled TiN powder and all acid leached residues appear as crystalline particles.

However, figure 15 shows that the particles, after vacuum distillation, have rounded edges and do not display the angular regularity found in the leached powder samples. The environment during the vacuum distillation altered the particles by removing the edges. No research was done to determine if this enhanced or detracted from the final use of the powder. Also, not all distilled powder displayed the rounded edges found in this micrograph. The exact conditions producing this effect are not known.

Three objectives were targeted in completing the particle size analyses of the TiN powder: determine the actual size of the powder, investigate the particle sizes collected at different points in the powder collection train,

Table 6.—TiN particle size analyses, TEM versus particle size analyzer

Powder sample	TEM					Particle size analyzer	
	Diameter, μm			Std dev, μm	Population size	Median diam, μm	Std dev, μm
	Max	Min	Mean				
Run 54:							
Distilled	0.31	0.04	0.10	0.05	431	0.13	0.04
Reactor	.28	.04	.11	.05	264	.13	.09
Run 56:							
Distilled	.29	.04	.11	.05	143	.17	.09
Reactor	.28	.04	.10	.04	304	.12	.16
Reactor receiver	.26	.04	.11	.04	457	.14	.09
ESP1	.23	.04	.11	.05	188	.13	.09
Scrubber	.25	.04	.11	.05	229	.15	.09

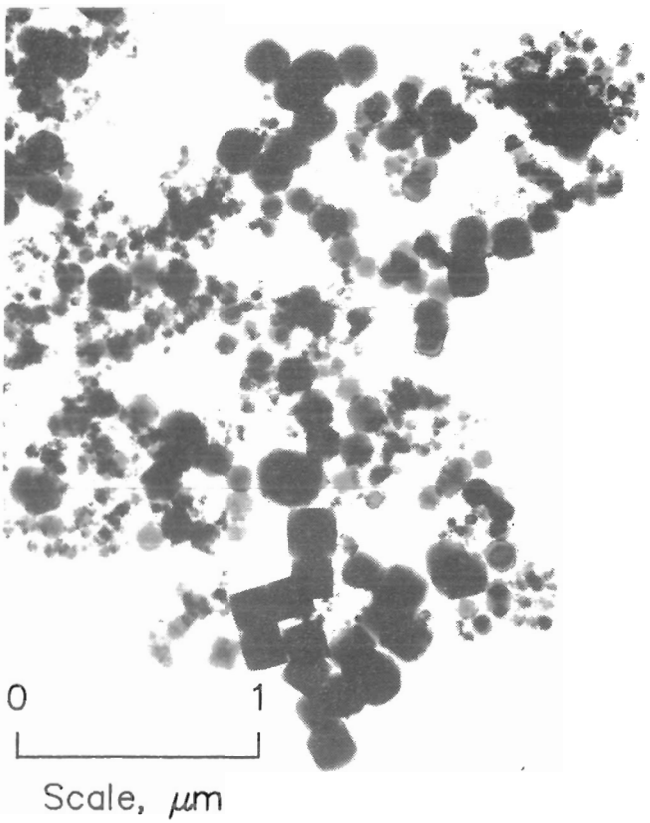

Figure 14.—TEM photomicrograph of leached TiN powder.

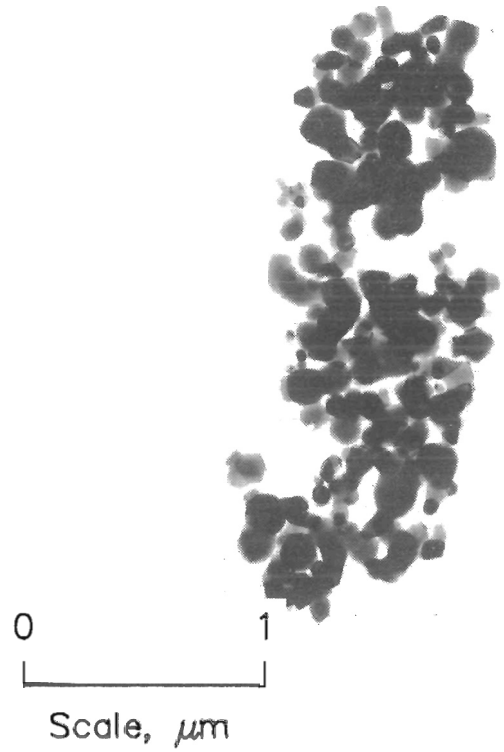

Figure 15.—TEM photomicrograph of vacuum-distilled TiN powder.

and determine if adjusting parameters affected particle size. Table 7 lists the median particle size and standard deviation of the TiN powders collected at various points in the reduction equipment and the distilled powder.

In analyzing the data in this table, several observations are apparent. With a few exceptions, the median particle sizes are very similar, which indicates the production of consistent particles in the vapor phase. The mean size of the distilled powder median diameters is 0.14 μm. This small size is a distinct advantage to the end user, since it is in the upper range of the nanometer powders desirable for certain aerospace applications. The standard deviations mostly range from 40 to 90 pct of the medians. Therefore, a narrow particle size range was not produced, but an improvement over most commercial powders was achieved.

The powder particle size at various points in the reduction equipment is important because collection could be optimized where the desired powder size is found. However, removing fine powder from a gas stream is difficult. Since the ESP1 powder had the smallest average median diameter, the quantity of powder collected in ESP2 was maximized. Analyzing the particle sizes at various locations in the reduction equipment is also important to determine if the vapor-phase reaction produces one or more particle sizes. The TEM photomicrographs showed three distinct particle sizes, but data in table 7 indicate that the particles were deposited at a consistent ratio everywhere in the system.

Producing the desired powder diameter would be very useful in a commercial process, and adjusting reduction parameters is the only possible method of changing the size. However, the data in table 8 show no statistical size difference among reduction runs. Within the ranges of the parameters tested, no change in particle size could be attributed to the change in conditions. Therefore, no control over powder diameter can be exercised.

TiN powder from the vapor-phase reaction did not yield a narrow particle size range, but did produce several specific sizes, as shown in the typical particle size distribution histogram (fig. 16). The majority of the particles were small, which would fill the voids between the larger particles. Improved packing density would occur if the proper mix of various particle sizes was present.

POWDER COMPACT EVALUATION

Another goal of the TiN powder research was to evaluate the powder in a compact. This was accomplished at the Bureau's Tuscaloosa Research Center in Tuscaloosa, AL, as part of the TiAlON research. The projected end

Table 7.—Particle sizes of TiN powders, diameter in micrometers

Run	Distilled powder		Reactor and ESP		Reactor receiver		ESP1		Scrubber	
	Median	Std dev	Median	Std dev	Median	Std dev	Median	Std dev	Median	Std dev
35	0.23	0.19	0.11	0.11	0.15	0.12	NS	NS	0.14	0.10
36	.15	.10	.18	.24	.16	.12	0.12	0.10	.19	.10
37	.14	.10	.13	.10	.12	.08	.11	.09	.16	.08
38	.11	.06	.11	.10	.11	.09	.12	.09	.10	.09
39	.15	.09	.13	.09	.13	.10	.11	.09	.13	.08
40	.11	.08	.11	.07	.14	.06	.11	.06	NS	NS
41	.12	.09	.13	.12	.12	.08	.12	.08	.13	.09
44	.10	.06	.11	.09	.12	.06	.11	.07	.08	.08
49	.10	.08	.10	.08	.10	.07	.10	.07	.09	.06
50	.16	.12	.12	.10	.11	.08	.10	.08	.14	.09
51	.12	.07	.12	.06	.12	.08	.10	.06	.11	.06
52	.15	.09	.15	.10	NS	NS	.09	.08	.11	.08
53	.13	.09	.10	.08	.12	.09	.11	.09	.09	.07
54	.13	.09	.13	.09	.14	.09	.12	.07	.12	.09
56	.17	.09	.12	.16	.14	.09	.13	.09	.15	.09
57	.10	.08	.11	.10	.10	.08	.08	.07	.12	.08
58	.12	.08	.12	.09	.11	.08	.08	.08	.11	.08
59	.12	.08	.12	.08	.12	.10	.09	.06	.13	.09
60	.12	.09	.13	.09	.11	.09	.10	.08	.09	.08

NS No sample.

Table 8.—Chemistries of distilled TiN powder used as component in TiAlON, weight percent

Sample	Ti	O	N	Mg	Cl	Fe	Cr	Ni	Al
Runs 26 and 28	71.3	1.19	18.9	1.21	0.27	2.94	1.09	0.048	NAn
Runs 29 and 30	73.7	.75	20.1	.30	.32	.19	.18	.009	0.03
High nitrogen	72.7	.54	21.7	.91	.32	.07	.11	NAn	.08
High-Mg	73.9	.89	20.4	1.21	.38	.07	.03	NAn	.27
Commerical powder (std)..	75.5	.71	21.9	.01	.07	.02	.11	.01	.25

NAn Not analyzed.

uses of the two materials are similar—wear-resistant parts and tool bits. The TiN powder prepared at the Bureau's Albany Research Center was substituted for the commercially available powder previously used. The properties of TiAlON were compared using four different Bureau-produced TiN powders with the same AlN and Al_2O_3 powders. Results were reported by Hoyer (*25*). These TiN samples contained different chemistries, as shown in table 8.

Each of the different TiN samples was turbomilled for 30 min with Al_2O_3 beads to break up any agglomerates. Commercial AlN and Al_2O_3 powders were added to obtain a 40-30-30 wt pct mix of TiN-AlN-Al_2O_3 and mixed for 30 min. The powders were dried before being passed through a 200-mesh screen. The mixtures were pressed hydraulically into 2-1/2- by 1-1/4- by 1/4-in briquettes before being pressed isostatically at 40,000 psig. Firing occurred in 5 psig N_2 at either 1,750° or 1,850° C for 2 h.

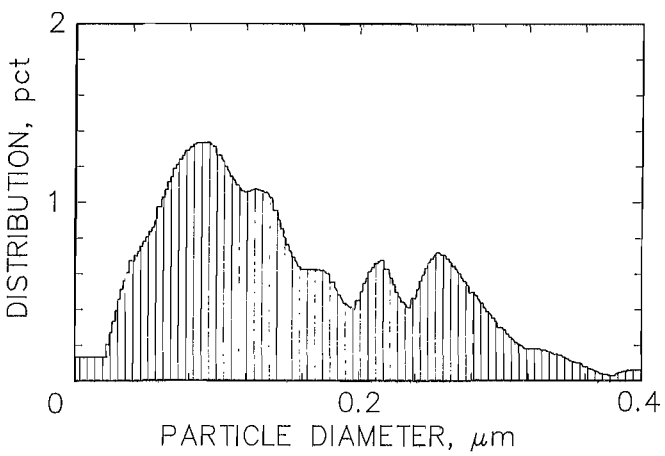

Figure 16.—Typical particle size distribution curve of TiN powder.

The resultant samples were measured for density, porosity, room-temperature modulus of rupture (MOR), and 1,000° C MOR. The Archimedes immersion technique in Hg was used to determine the bulk density (reported as density) (*26*). True density was measured with an autopycnometer. Porosity was calculated using the following formula:

$$\text{pct porosity} = \frac{d_t - d_b}{d_t} \times 100,$$

where d_t = true density, g/cm^3,

and d_b = bulk density, g/cm^3.

The MOR specimens were broken using a four-point bend fixture. The results are shown in table 9 and compared to a standard that used commercially available TiN powder.

The results show improved density, porosity, and room-temperature MOR, with increased firing temperature for the Bureau's TiN samples. The results also show that the Bureau-produced TiN powder yielded improved properties over that of the standard sample at the same firing temperature despite higher impurities, especially oxygen, Fe, Mg, and Cr. These impurities could have resulted in impaired properties for certain applications, but not for TiAlON. In fact, the different levels of impurities, as found in the Bureau's TiN samples, produced no difference in the measured properties. The high-temperature (1,000° C) MOR using the Bureau's TiN sample in TiAlON was similar to that in which the standard TiN was used.

Two explanations could help clarify these results. First, the properties are measured on TiAlON composites, which depend upon oxygen as introduced in Al_2O_3. This negates some of the effect of introducing impurities. Second, the Bureau's TiN has a much smaller diameter (0.14 μm) than the standard (4.6 μm). The smaller size could produce a more homogeneous composite, which results in improved properties. Perhaps this outweighs the disadvantage of increased impurities.

Table 9.—Properties of TiAlON composites using Bureau-produced TiN powder

Sample	Firing temp, °C	Density, g/cm^3	Porosity, pct	MOR, MPa	
				Room temp	1,000° C
Standard	1,850	3.7	17.8	201	258
Runs 26 and 28	1,750	3.06	27.7	121	NAn
Do.	1,850	3.88	9.2	251	NAn
Runs 29 and 30	1,750	2.96	25.5	134	NAn
Do.	1,850	3.93	8.9	252	NAn
High-nitrogen	1,750	2.82	25.9	142	NAn
Do.	1,850	3.31	16.6	265	250
High-Mg	1,750	2.82	23.1	141	NAn
Do.	1,850	3.59	9.7	290	253

NAn Not analyzed.

CONCLUSIONS AND RECOMMENDATIONS

This research successfully produced high-nitrogen TiN powder. A low-pressure, relatively low-temperature reaction scheme, utilizing a known process (Kroll process), was used. Powder-collecting techniques based on a simple ESP were successful. The powder was purified by thermal vacuum distillation without introducing additional impurities. These known techniques, combined with meticulous procedures and handling, produced the desired submicrometer powder in a system that could be run continuously.

A large-scale reactor was used to prepare TiN powder via vapor-phase reactions. The powder produced had enhanced properties and reduced impurity levels when compared to powder from the small-scale reactor. Nitrogen levels were increased. Contaminants included metals, reaction products (Mg and Cl), and oxygen. The metal impurities were reduced by changing the materials of construction from Fe-based alloys to Al_2O_3. The Mg and Cl contents were reduced slightly by increasing the vacuum distillation temperature and duration. However, much more needs to be done to reduce these reduction products. Oxygen levels were decreased in the TiN powder by feeding purer reactants, using cleaner equipment, and eliminating contact with air. Distilled TiN powder consistently displayed <0.6 wt pct oxygen.

The nitrogen content of the distilled TiN powder was used as an indication of the effect of changing parameters with a stoichiometric amount of 22.6 wt pct nitrogen as the goal. Baffles were used in the reaction zone to increase reactant contact, which increased the nitrogen content slightly. Elevated amounts of the Mg reductant also increased the nitrogen content, as did reacting NH_3 instead of N_2. However, the greatest improvement resulted when $TiCl_4$ was vaporized before introduction into the reactor. This ensured completely vaporized reactants. Consequently, TiN nitrogen levels could be maintained near 22.0 wt pct. The rate of feeding NH_3 and $TiCl_4$, reaction zone temperature, and reaction zone residence times had no significant effect on the nitrogen content in the TiN powder. However, since changing one parameter often affected another, the precise influence on nitrogen content was often difficult to ascertain.

A material balance showed that over 94 wt pct of the Ti was reacted and accounted for. However, only about 50 wt pct was recovered in a usable TiN powder form.

50 wt pct was recovered in a usable TiN powder form. This percentage could be increased by operating the equipment longer, which would reduce the fraction trapped in the reactor and lines.

Distilled TiN powder particle sizes averaged 0.14 μm in diameter with a standard deviation of 0.09 μm. Some minor size segregation occurred in the reactor and powder collection train, but the particle size was unaffected by the different parameters. The standard deviation indicated that a narrow particle size range was not present. However, several different sizes were predominant, which could aid packing densities.

Composites of TiAlON using Bureau-produced TiN resulted in improved properties over commercial TiN. Increased density and MOR and decreased porosity were measured. Impurities in the TiN, over the range tested, did not effect the property values.

Based on successful TiN production by vapor-phase reactions, similar operation of the equipment could also produce other powders, such as Ti, TiC, AlN, etc., from chlorinated reactants. Further research is needed to reduce oxygen and Mg contents and to study the suitability for producing TiN composites.

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